TAILORED FISCHER-TROPSCH SYNTHESIS PRODUCT DISTRIBUTION

RELATED APPLICATIONS

This is a divisional of U.S. patent application Ser. No. 10/911,976, now abandoned, filed Aug. 4, 2004 which claimed priority to U.S. Provisional Application No. 60/493,094, filed Aug. 5, 2003.

This invention was made with Government support under Contract DE-AC0676RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

This invention relates to Fischer-Tropsch synthesis and especially Fischer-Tropsch synthesis of liquid hydrocarbons.

INTRODUCTION

In Fischer-Tropsch synthesis, liquid hydrocarbon fuels are produced from lighter gases. This process was first put to large-scale industrial use by Germany during World War II. Since that time, many chemists and chemical engineers worked to develop improvements to the process. There continues to be intense academic and commercial interest in improving Fischer-Tropsch synthesis because it offers a source of liquid hydrocarbon fuels in addition to the increasingly costly process of extracting oil from the ground. Furthermore, Fischer-Tropsch synthesis could make a significant beneficial environmental impact by capturing methane and other greenhouse gases that might otherwise be released from remote oil wells.

A problem with Fischer-Tropsch synthesis is that it is difficult to control the products resulting from the synthesis. In a series of patents assigned to Exxon, Fischer-Tropsch catalysts were described in which the active catalyst was dispersed around the rim of a catalyst particle. For example, in U.S. Pat. No. 5,128,377 the inventors suggested a surface film of cobalt having a thickness generally ranging from about 0.02 mm to about 0.20 mm, preferably from about 0.04 mm to about 0.20 mm, disposed on particles ranging in diameter from about 0.5 mm to about 2 mm. Similarly, in U.S. Pat. No. 5,140,050 the inventors suggested that the catalytically active cobalt be dispersed in a catalytically active surface layer ranging in average thickness from about 20 microns to 250 microns, preferably from about 40 microns to about 150 microns. Gimpel et al. in WO 02/07872 suggested a preferred range of 5 to 80 microns for the outer layer of catalytically active metal. In each of these cases, the catalyst particles are used in fixed bed or slurry-type reactors. Iglesia et al. in "Reaction-Transport Selectivity Models and the Designer of Fischer-Tropsch Catalysts," modeled Fischer-Tropsch synthesis over rim-type catalysts and provided an equation to calculate the optimal thickness of the catalytically active layer to obtain the minimum methane selectivity.

A few workers have described systems for Fischer-Tropsch synthesis that do not require fixed bed or slurry-type reactions. For example, Schanke et al. in U.S. Pat. No. 6,211,255 described Fischer-Tropsch synthesis through washcoated microchannels of a honeycomb reactor. The inventors did not describe the thickness of the washcoat, nor the distribution of liquid hydrocarbon components in the product. Based on the modeling of Iglesia et al, it would be expected that, in the structure of Iglesia et al., the optimal methane selectivity would require a relatively thick catalyst washcoat.

Wang et al., in U.S. Pat. No. 6,558,634, stated that in order to mitigate the mass transfer limitations of the catalyst structure, the catalyst impregnation preferably forms a porous interfacial layer having a depth less than 50 μm, preferably less than 20 μm, and commented that the thinner impregnated catalyst structure also enhances heat transfer due to a shorter heat transfer pathway, and leads to lower selectivity to methane. Reactors are described in which a porous, contiguous catalyst is placed in a microchannel.

SUMMARY OF THE INVENTION

The inventors have surprisingly discovered a method of Fischer-Tropsch synthesis that results in a superior product mixture of liquid hydrocarbons which, compared to prior art processes, has a relatively high ratio of C_5-C_{20}:C_{20+}. In this method, the reactants are contacted over a Fischer-Tropsch catalyst that has a catalytically active surface layer having a thickness of 35 microns (μm) or less. Preferably, in this method, the catalyst is disposed in a microchannel (or microchannels) that has a bulk flow path extending over the entire length of the microchannel.

The invention includes methods of Fischer-Tropsch synthesis, Fischer-Tropsch catalysts, and reactors containing the catalyst. The invention also provides novel hydrocarbon compositions.

In a first aspect, the invention provides a method of decoupling methanation from synthesis of liquid hydrocarbons in a Fischer-Tropsch process, comprising: contacting H_2 and CO in a reaction microchannel over a catalyst at a temperature sufficient to convert the CO to hydrocarbons; wherein there is a bulk flow path past the catalyst and the catalyst has a thickness of catalytically active component that is less than 35 μm; wherein the catalytically active component comprises a Fischer-Tropsch catalytic metal; and wherein the method has the characteristic that, while maintaining other reaction conditions, adjusting reaction temperature can increase CO conversion (absolute) from 25% to 60% while methane selectivity increases by less than 80% (relative) over the same temperature range and conditions.

In another aspect, the invention provides a reactor for Fischer-Tropsch synthesis, comprising a microchannel and a catalytically active surface layer disposed over at least a portion of the surface of the microchannel. The catalytically active surface layer comprises a Fischer-Tropsch catalytic metal and wherein the thickness of the catalytically active surface layer is less than 35 μm. Preferably, there is a bulk flow path through the microchannel. In some preferred embodiments, the thickness of the catalytically active surface layer is less than 20 μm, and in some embodiments in the range of 2 to 20 μm. In some embodiments, the microchannel is in a honeycomb.

The reactor (and/or the inventive methods) can also be characterized by reactivity described in the examples. For example, having methane decoupling selectivity such that when hydrogen and carbon dioxide are fed into the reactor at a H_2:CO ratio of 2 and a weight hourly space velocity of 3.73 g CO/g catalyst/hr, a combined (H_2+CO) feed pressure of 40 atm, and temperature is increased from 224° C. to 260° C., the CO conversion more than doubles while the methane selectivity increases by 70% or less.

In a further aspect, the invention provides a method of making a hydrocarbon composition via the Fischer-Tropsch synthesis, comprising: contacting H_2 and CO over the catalytically active surface of the reactor of the second aspect, at a temperature sufficient to convert the CO to hydrocarbons. Preferably, there is a contiguous bulk flow path through the